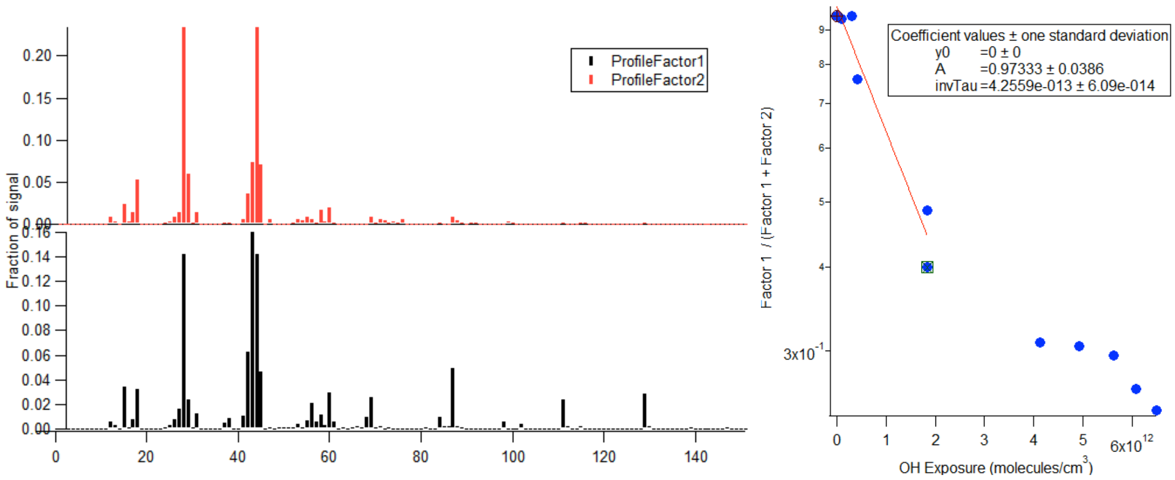
Review of **“Application of positive matrix factor analysis in heterogeneous kinetics studies: an improvement to the mixed-phase relative rates technique”** by Liu et al.

This paper describes an approach for analyzing laboratory data on the heterogeneous oxidation of organic submicron particles. The authors point out that the use of hard ionization mass spectrometry can lead to biases in the inferred kinetics, since product ions may interfere with reactant ions. They thus recommend the use of positive matrix factorization (PMF) rather than spectral subtraction (which involves using the fastest-decaying ion) for deriving kinetic parameters. Applying this approach to the heterogeneous reaction between gas-phase OH and particulate citric acid, they measure an uptake coefficient that is ~8 times faster than what we had measured previously (Kessler et al., 2012, hereafter K2012).

This is an interesting new approach, on a topic of importance to the atmospheric chemistry community. It makes a fairly strong prediction, that the reanalysis of AMS-based heterogeneous oxidation experiments will lead to faster inferred kinetics (which in turn lead to shorter inferred atmospheric lifetimes of the particulate organics). However, as described below, using this technique on our own data, we are unable to see such an enhancement. Thus the primary conclusion of the study appears not to always be the case; thus before it can be published in ACP, this paper needs to be rewritten considerably.

Major comments:

(1) We ran PMF on the (UMR) mass spectrometric data of K2012, for the citric acid oxidation case. Results are shown below:



Left panels: mass spectra of the two PMF components determined, products (top) and citric acid reactant (bottom). Right panel: decay kinetics of the citric acid factor. As in K2012, the initial slope (“invTau”) gives the second-order rate constant.

As in the present study, two factors (right panels) were found; however these factors (which represent ~99% of the variance of the data) look substantially different from one another. Fitting the decays (right panel) yields a second-order rate constant of k=4.3x10^{-13} cm^3 $molec^{-1}$ s^{-1}. This is in excellent agreement with our previous analysis, using the fastest-decaying ion ($C_4H_4O^+$, *m/z* 68.03), and is far lower the rate constant determined from PMF in the present study. Thus the difference in results in the two studies does not derive from the choice of analysis approach taken in K2012. The present manuscript needs to be rewritten to reflect this.

(2) Such differences in kinetics are perhaps not surprising given a major difference in reported results: the ion at *m/z* 68 was the fastest-decaying one in the K2012 but did not change appreciably in the present study. The authors attribute this difference to the 10K difference in experimental temperatures; however going from ~60% loss (K2012) to ~0% loss (present study) of a compound would require an enormous change in volatility (something like a 100x increase in vapor pressure), and is unlikely to arise from such a modest temperature difference. Instead other factors are likely to be at play, and these should be discussed in the present paper. Two possibilities include

(a) the oxidation chemistry could be different. Differences in the oxidation conditions (ratios of O3/OH/HO2/hv) could lead to fundamental changes in the observed chemistry.

(b) the physicochemical properties of the particles could be different. Citric acid is a solid at room temperature, likely to form nonspherical particles and/or glasses upon atomization. Differences in the particle phase/shape could have a dramatic influence on the chemistry/dynamics on/within the particles.

These are important topics that probably deserve more investigation than they have received in the literature so far.

Other points

- A distinction between unit-mass resolution (UMR) aerosol mass spectrometry and high-resolution (HR) aerosol mass spectrometry needs to be made in this paper. The present manuscript utilizes UMR mass spectra only, whereas K2012 (and others) used HR spectra. Such a difference is unlikely to affect results for citric acid – the PMF analysis presented above is for our mass spectra at UMR – but is nonetheless important, given that HR analysis provides an extra level of distinction between different chemical species. Right now the UMR-HR difference is not mentioned at all in the present manuscript.

- The authors make the important distinction between soft and hard ionization for tracking decay of individual particulate organic species (p. 8698, line 17-25). Soft ionization is clearly preferable; however for one system we have made a direct comparison between results from the two (Figure 5 of Smith et al. 2009). For that system (squalane+OH) the two compare extremely favorably (at least when high-resolution EI peaks are used). Of course the agreement may not be as good for other chemical systems, but this result shows that the use of EI peaks may not be as fundamentally problematic as suggested in the present manuscript.

- P. 8707, line 11-12: the argument that the use of larger fragments results in larger derived values of k may be true in the present study, but is not always the case; for example the ion used in K2012 ($C_4H_4O^+$ for citric acid) was chosen because it decayed away faster than all the other major peaks, including higher-mass ones.

- Mathematically, the only way that a PMF-factor-derived rate constant can be faster than the decay constant of any constituent ion is if the two PMF factors (assigned to products and reactants) are very similar. The authors argue that this is indeed the case in the present system, as shown in Figures 3-4 (and justify this in Schemes 1-2). However, this requires a very high degree of confidence in the PMF results. Here, the two factors account for only ~85% of the variance in the mass spectrometric data, which is extremely low – there is a good deal of residual mass spectrometric signal that is unaccounted for. This remaining 15% variability is on the order of the change in the intensity of the individual ions (see fig. 5c), making it extremely difficult to make any solid conclusions about the chemistry based on these PMF results alone.