

Response to Referee 1

Overall, the FIGAERO-HR-ToF-CIMS measurements of toluene SOA that were added to the revised manuscript significantly strengthen proof of principle for application of the APPA to study aqSOA formation. The specific discussion of those results would benefit from some clarification text and additional analysis that I suggest below. Once these comments are addressed, I would support publication of the manuscript in AMT.

We are very thankful for the recommendations of changes and additions provided by the referee.

Comments specific to FIGAERO-HR-ToF-CIMS data presentation and interpretation

1. L638-641: I suggest rewriting this text for greater clarity/conciseness, something like: “Filter Inlet for Gases and Aerosols (FIGAERO) coupled to an iodide adduct High-Resolution Time-of-Flight Chemical Ionization Mass Spectrometer (FIGAERO-HR-ToF-CIMS; Aerodyne Research, Inc.)”

The sentence was revised as suggested.

2. L676: Replace ‘CIMS’ with ‘FIGAERO-HR-ToF-CIMS’

The acronym was replaced as suggested.

3. L677-684: I suggest rewriting these sentences for clarity/conciseness, something like: “The signal observed at $m/z = 217$ ($C_2H_2O_4I^-$) was absent from the mass spectrum obtained from SOA generated in the APPA at 40% RH (Fig. S7a) but was the dominant peak in spectra obtained from SOA generated at 85 and 100 % RH (Figs. S7b and c). The $C_2H_2O_4I^-$ signal corresponds to oxalic acid, which can be produced following reactive uptake, hydration, and multi-generational OH oxidation of glyoxal in the aqueous phase (Lim et al., 2010). While glyoxal is a major gas-phase OH oxidation product of toluene (Volkamer et al., 2001), oxalic acid is not generated via subsequent gas-phase OH oxidation of glyoxal (Warneck, 2003), which is why it is observed in Figs. S7b-c but not in Fig. S7a.”

The sentences were revised as suggested.

4. Figure S7 and related discussion.
 - a. Add (a), (b), and (c) labels to the mass spectra obtained at 40%, 85%, and 100%, respectively.

The labels were added.

- b. Add OH exposure values at which Figure S7a, b and c were obtained - this information is critical to properly interpret results in the context of the SOA yields presented in Fig. 12 - and reference the corresponding OH exposure values in the Sect. 3.2.1 discussion.

The first sentence in the Figure S7 caption is now:

“Mass spectra of SOA produced from OH-oxidation of toluene in the presence of dry seed particles (40 % RH), aqueous seed particles (85 % RH), and cloud droplets (100 % RH), with OH exposures calculated from KinSim of 1.06×10^{12} , 1.03×10^{12} , and 1.01×10^{12} molec. cm^{-3} s, respectively.

- c. Please extend the FIGAERO-HR-ToF-CIMS spectra to show signals down to $m/z = 200$, which would then include known aqueous phase glyoxal oxidation products at $m/z = 201$ ($\text{C}_2\text{H}_2\text{O}_3\text{I}^-$, glyoxylic acid) and/or 203 ($\text{C}_2\text{H}_4\text{O}_3\text{I}^-$, glycolic acid), both of which are detected with iodide adduct CIMS at even greater sensitivity than oxalic acid (e.g. Table S1 in Lee et al., 2014).

The x-axes were extended down to $m/z = 200$. As you will see, no additional peaks are evident.

- d. Glyoxylic acid is a direct precursor to oxalic acid via aqueous phase OH oxidation (e.g. Lim et al., 2010). It would be especially noteworthy if the $\text{C}_2\text{H}_2\text{O}_3\text{I}^-$: $\text{C}_2\text{H}_4\text{O}_3\text{I}^-$ ratio is higher at 85% RH than 100% RH, for example. If glyoxylic/glycolic acid signals are not present, it could be because they were already fully consumed at the OH exposures that were used, in which case that could be briefly discussed in the text.

As noted above, peaks corresponding to glycolic and glyoxylic acid are not evident in the extended spectra. The following was added to the text to explain this observation:

“Peaks are not evident in the spectra corresponding to glyoxylic acid ($\text{C}_2\text{H}_2\text{O}_3\text{I}^-$; $m/z = 201$) and glycolic acid ($\text{C}_2\text{H}_4\text{O}_3\text{I}^-$; $m/z = 203$), both of which are oxidation products of glyoxal and the former of which is a direct precursor to oxalic acid through aqueous phase oxidation (e.g., Lim et al., 2010). The absence of those compounds together with the high concentration of oxalic acid is attributed to a combination of their oxidation to near completion during the ~8-day equivalent photochemical aging in the reactor and to their evaporation from the residual particles following evaporation of the water from the droplets because of their substantially higher vapor pressures (~1 mmHg, ~0.02 mmHg, and 0.0002 mmHg for glyoxylic, glycolic, and oxalic acid, respectively; Brown, 2008).

- e. Figure S7 shows the intensity of FIGAERO-HR-ToF-CIMS signals obtained from $m/z = 210-360$ normalized to $C_3H_2O_4I^-$ (Fig. S7a) or $C_2H_2O_4I^-$ (Figs. S7b-c). While this may be adequate for the sole purpose of showing that $C_2H_2O_4I^-$ is either present or not, it would be a much clearer presentation if the ion signals were normalized to the calculated mass of SOA collected on the filters – which could be estimated from the SOA mass concentration measured with AMS or SMPS. This would then more closely relate the abundance of specific ions that were measured to the SOA yields that are plotted in Fig S12. For example, while the mass spectra of SOA generated at 85% RH and 100 % RH look similar, the SOA yield is up to a factor of 2 higher in the 100% RH case. Why is that - are the same products generated in both cases, in different yields? It's impossible to tell the way the data are currently presented.

The spectra are now normalized by the collected SOA mass.

Other comments

5. L595: for context, I suggest indicating that the OHR_{ext} from 150-250 ppb of added SO_2 is approximately $0.5-0.8 s^{-1}$.

I calculate a range of $4.7 - 7.8 s^{-1}$. Below is the approximate calculation for 150 ppb.

$$OHR_{ext} = (1.3 \times 10^{-12} cm^3 s^{-1})(150 \times 10^{-9})(2.4 \times 10^{19} cm^{-3}) = 4.7 s^{-1}$$

Nevertheless, that range is included in the modified sentence:

“For the simulations resulting in the values along the upper (black) curve, the only source of “external” OH reactivity (OH_{ext}) (Peng et al., 2015) was the ~ 4.7 to $7.8 s^{-1}$ corresponding to the added 150 to 250 ppb SO_2 .”

6. L606-621 and Figure 10: This content should either be deleted or moved to the supplement – while interesting and showing that the authors’ OH exposure calibration studies were done carefully, the discussion of this result/trend is not specific to the APPA and is more of a commentary on the use of OH tracers whose products can also react with OH.

The paragraph and figure were moved to the supplement. The following sentence was added to the end of the previous paragraph:

“A summary of the measurements and simulations for high RH experiments using benzene is provided in Supplement 5 and Fig. S7.”

7. Figure 6 is missing (a) and (b) labels.

They were actually in there, but positioned above the graphs (and not very easy to see). They are now moved inside the graphs.

8. In Figure 6(b), the “well-stirred” RTD trace looks black, whereas the legend trace indicates it should be light grey.

The colors are now correct.

References

Lim, Y. B., Tan, Y., Perri, M. J., Seitzinger, S. P., and Turpin, B. J.: Aqueous chemistry and its role in secondary organic aerosol (SOA) formation, *Atmos. Chem. Phys.*, 10, 10521–10539, <https://doi.org/10.5194/acp-10-10521-2010>, 2010.

Lee, Ben H., Lopez-Hilfiker, Felipe D., Mohr, Claudia, Kurtén, Theo, Worsnop, Douglas R., and Thornton, Joel A. An Iodide-Adduct High-Resolution Time-of-Flight Chemical-Ionization Mass Spectrometer: Application to Atmospheric Inorganic and Organic Compounds. *Environ. Sci. Technol.*, 48, 11, 6309-6317, <https://doi.org/10.1021/es500362a>, 2014.

The Lim et al. reference was already included. We did not include the Lee et al. reference because it did not seem necessary to comment on the relative ionization efficiencies when no peaks corresponding to glycolic and glyoxylic acid are evident in the spectra.