

## **Final Author Comments on “A switchable reagent ion high resolution time-of-flight chemical ionization mass spectrometer for real-time measurement of gas phase oxidized species: characterization from the 2013 Southern Oxidant and Aerosol Study”**

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We would like to thank both anonymous referees for their comments and their time spent in reviewing this manuscript. Some of our own concerns were reinforced by referee comments and other new ideas have given us additional direction/reinforcement of the importance in analytical evaluation of these complex measurement systems. We have plans of writing a future manuscript to address various science questions relevant to oxidation chemistry in the Southeastern United States within the scope of the numerous CIMS measurements conducted during SOAS.

### **Response to Anonymous Referee #2: Specific Comments**

#### 1. Formic Acid Calibrations and Other Species

Referee Comment:

*I understand why the authors opted to only quantify formic acid from their field data since they had a calibration in place for it. However, since acetate CIMS is highly selective to organic acids, I wonder why not use its calibration factor to quantify the other organic acids? Have the authors tried exploring how different the response factors are between different organic acids in the lab? Many of the acids are commercially available that you detect from the field. I would think you could devise a way to see how different they really are in the lab. If you don't expect the response factors to vary that much (say less than a factor of 2-3), then maybe it is reasonable to quantify the other organic acids and apply the uncertainty to the value? I agree with the point made by the authors though that the time series of the unquantified data itself is useful to understanding potential reactions or sources of these compounds.*

I generally agree that when we calibrate this system, we see fairly low variability in the sensitivities determined in the field and in the laboratory. We have only recently started to work through the calibrations of commercially available acids, and we are in the process of an additional publication related to instrument response and data interpretation. All these calibrations must be done using permeation tubes or newly emerging liquid calibration systems, which are extremely time consuming.

The formic acid time series was adjusted on an hour basis to compensate for changes in sensitivity. While not the dominate driver of instrument instability (zeros are the main issue), we believe the attention paid to a single compound is the importance point to be made. Calibrating hourly for formic acid and then applying a single point calibration for other organic acids of

interest based off one real calibration seems to reduce the suggestion that calibrations in the field are necessary for high quality quantification possible with these systems.

See comment Response to Anonymous Referee #1 Substantial Comments #1

## 2. Isoprene Oxidation Products

Referee Comment:

*How did MAE's time series compare with isoprene and IEPOX/ISOPOOH data? Was there a correlation with these? Also, since NO<sub>x</sub> appears to play a role in which products are favored, would the authors consider using collocated data from their SOAS site to explore these connections further? I wonder if the authors have plans to further explore this in subsequent work. I know that this isn't the primary focus here.*

We have the intention of beginning work to try and tie together the general observations from SOAS using CIMS and PTR measurements at the SOAS "Super Site"; this recommendation is beyond the scope of the analytical work presented here. Isoprene related compounds in the intermediate volatility range (ISOPOOH/IEPOX, MAE) are only one set of compounds observed that are related to the oxidation of isoprene. More oxidized species with extremely low volatility are also observed. This is also true for alpha-pinene and beta-pinene. The incredible number of HR-TOF-CIMS instruments in various configurations co-located during SOAS necessitates this occurs, but this is far outside the scope of presenting the switching reagent CIMS and discussions of field deployment.

## 3. Monoterpene Oxidation Products

Referee Comment:

*Monoterpene oxidation products: Similar to # 2 above, for the monoterpene products, was there any relation to monoterpenes or their products from PRTMS other methods at this site?*

See comment #2 directly above in this section.

## 4. RH Effect on Iodide

Referee Comment:

*I'm curious as to why the authors didn't more carefully examine RH effect with zero air and with some standard compounds with iodide CI in the lab? Could this provide insights into field operation with high purity zero air?*

We have not been primarily focusing on iodide calibrations due to the complexities associated with humidity dependence. Other groups have published careful calibrations with iodide since the SOAS study highlighting these complexities, and we refer the referee to Lee et. al. in Environ. Sci. Technol. 2014, 48, 6309-6317. The effect was more extreme, and more complex, than we assumed it would be when trying this switching approach.

The main message about iodide and acetate used together as reagent ions is that acetate measurements did not appear to be affected by running iodide every other hour. There are certainly many additional caveats and intricacies to either of these reagents (relative humidity being one of them).

### **Response to Anonymous Referee #2: Minor Comments**

1. We will change all instances of “isoprene hydroperoxide” and “isoprene epoxide” to “isomeric isoprene hydroperoxides” and “isomeric isoprene epoxydiols”.
2. We will change all instances of “South East” to “southeastern”
3. It is of our opinion that figures 6 and 7 are of extraordinary importance to the analytical rigor of what we set out to show with this instrument. It is one thing to show that a single component calibration (formic acid) does not have humidity dependence as past publications with acetate have done, and it is another to show that whole air matrix effects do not bias formic acid measurements. This is sharply contrasted by the results with iodide that show strong biases in the two calibration/background methods. We also want to present the aspects of this experiment that did not work alongside the aspects of this experiment that did work.