The black color of the text in this document shows the reviewer's comments, while the green color shows the authors' responses, and the revised text is shown in italics.

In this manuscript, Riva et al. introduced a newly developed medium-pressure chemical ionization reactor, Vocus AIM, utilizing adduct ionization for the detection of gaseous inorganic and organic compounds. The performance of the Vocus AIM reactor in terms of time response, sensitivity, and selectivity under different ionization schemes was characterized using selected inorganic and organic species, as well as experiments of alpha-pinene ozonolysis. The novel design of Vocus AIM significantly improves the time response of instrument, enables sensitive detection of a range of inorganic and organic species in sub-ppt level, and effectively eliminates the water vapor dependencies of the sensitivity by introducing an appropriate dopant. In addition, by combining multiple ionization schemes with different selectivity, the Vocus AIM is able to measure organic compounds spanning a wide range of volatility and oxygenation level. This work is scientifically sound and the manuscript is nicely written. I recommend its publication in AMT after the following comments are addressed.

We thank the reviewer for his/her careful consideration of our article. We have attached a revised version of the manuscript in which we considered all the comments raised by the reviewer.

L186-188: I would expect that the reagent ion current is affected by the mixing ratio of benzene with other reagent ion precursors. Do the authors have any recommendations for those mixing ratios?

The choice of the reagent ions should be made to avoid any interference. In the case of the example mentioned by the reviewer, methyl iodide or bromo ethane are not detected by benzene chemistry even at mixing ratios ranging from 0.1-10 ppm. Some other cases would be more problematic, e.g., running the Vocus AIM reactor using benzene and acetone-NH_4^+ chemistries. Indeed, the large quantity of NH_3 injected within the AIM reactor will be detected by benzene cations and will ultimately impact the TIC. Overall, the compatibility of ion chemistry in the AIM system is determined by whether a generated reagent ion can detect the neutral precursors from any other attached ion source. Therefore, reagent ions should be chosen to avoid any interference. For instance, the combination of Iodide, Benzene, and acetone ion chemistry works effectively even at gas mixing ratios of 1 ppm for benzene and 3 ppm for acetone. This demonstrates that these chemistries can coexist without significant interference, allowing for accurate detection and measurement.

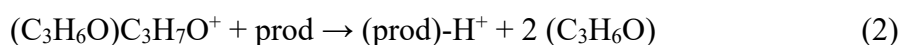
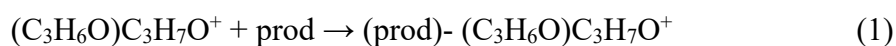
We have added the following sentence.

Lines 189-191: *"The compatibility between multiple ion chemistries in the AIM system is determined by whether a generated reagent ion can detect the neutral precursors from any other attached ion source."*

L212: In the protonated acetone dimer ionization chemistry, are the species mainly ionized by adduct formation or proton transfer? How does the relative contribution of these two ionization pathways depend on the molecular properties of analytes?

In the case of protonated acetone, both mechanisms i.e., adduct formation and proton transfer occurred. This depends on multiple aspects, including the proton affinity of the analytes, the stability of the adduct, and the energy the ions might experience when traveling through the ion optics. Hence the ionization mechanism proceeds according to the following equations:

$$(C_3H_6O)C_3H_7O^+ + prod \rightarrow (prod)\text{-} (C_3H_6O)C_3H_7O^+ \qquad (1)$$

$$(C_3H_6O)C_3H_7O^+ + prod \rightarrow (prod)\text{-}H^+ + 2\,(C_3H_6O) \qquad (2)$$

The stability of the adduct is governed by the polarizability of the analytes (i.e., functional groups). In general, the more the molecule is functionalized the more likely adduct formation will be the prevalent ionization process. This mechanism is not only valid for acetone dimers but general to positive ion chemistry involving protonated reagent ions.

L261-263: Was the sensitivity of protonated acetone dimers to levoglucosan also measured? If so, the relevant results should be presented and discussed in the manuscript.

Levoglucosan was not measured in this ion chemistry due to its known reaction at the collision limit with iodide (Lee et al., 2014), which we utilized for calibration purposes. Therefore, we did not explore alternative ion chemistries for this molecule.

L385: Please provide the sensitivity deviation value for formic acid and nitric acid.

This has been updated within the new version of the manuscript:

Lines 387-389: *"With acetonitrile as the dopant, the change in sensitivity across the humidity range is reduced to a deviation of <20% relative to dry conditions for all model compounds, more for formic acid and nitric acid (<10 %)."*

L402: What are the typical reagent ion currents for chloride and ammonium ionization schemes? Also, what are their sensitivities and LoDs toward the calibration standards used in this study?

The typical total ion currents for Chloride and Ammonium reagent ion chemistries are generally 1-2 and 3-6 x 10^6 ions/second. The lower reagent ion current of Cl chemistry is explained by the BSQ settings that greatly reduce the transfer efficiency of ions below m/Q 50 th. In our study, we did not perform calibration using the Chloride reagent ion chemistry. Acetone-NH_4+ ion chemistry does not exhibit sufficient sensitivity to detect the specific species chosen as calibrants in this manuscript. Instead, we routinely calibrate Vocus AIM for this mode using methyl ethyl ketone (MEK) via cylinder, achieving normalized sensitivities of 5 ncps/ppt, with a corresponding LoD of 4.8 ppt (60 s). Values have been added to Table 1

L410: How the limit of the detection is determined should be described in the manuscript.

The following sentences have been added to mention how LoDs were determined:

Lines 415-418: *"LoD measurements were performed by introducing 2 SLPM of dry UHP N2 (i.e., background measurement) for 10-15 minutes. The LoD was estimated by using Tofware and calculating the Allan variance (i.e., the stability of the signal over time). Finally, the LoD corresponds to 3-standard deviations (sigma) of the Allen variance and is determined as a function of integration time estimation."*

L455: In the ammonium ionization scheme, protonated acetone dimers are also present. Were any organic compounds ionized by protonated acetone dimers, via adduct formation or proton transfer?

In the ionization scheme, acetone dimer formation is hampered by the large presence of ammonia (NH_3). It should be noted that, if the NH_3 concentration is below $\sim$ 100 ppm, multiple ionization processes might occur, including mechanisms involving protonated acetone dimers. A sentence has been added to clarify this aspect.

Lines 209-211: *"If the concentration of NH_3 is lower than 100 ppm, multiple ionization processes might occur (e.g., acetone dimers, charge transfer,…) which would complicate the mass spectrum analyses."*

This has been corrected in the new version of the manuscript

We agree with the reviewer, and we have revised the labels as suggested.