

Here we copy over the comments of Reviewer 1 for our preprint, with our responses to each in red bullet points. We greatly appreciate the discussion and points raised.

The authors describe an updated design of a transverse atmospheric pressure Ion Molecule reaction Region (t-IMR) for use with chemical ionization mass spectrometers (CIMS). The authors describe in detail the details of operating and optimizing this t-IMR and demonstrate the capability of measuring trace gases at a ground site in the marine boundary layer. The data presented in this manuscript is quite impressive for difficult to measure sticky trace gases such as HOBr and HNO₃, and should be published. I have concerns about how the instrument could be calibrated for analytes difficult to deliver in the field, as the IMR conditions are not held constant (i.e. water vapor, pressure) during deployment and would require chamber experiments at field conditions in order to measure sensitivity as a function of these conditions. I would like to see the data for IH₂O/I included in this manuscript to make the operation conditions of this system clearer to other users.

- We have added a figure to the appendix showing representative changes in I- and IH₂O- ion signals during the BLEACH23 campaign. We agree that by not holding IMR conditions (i.e. humidity) constant, this creates the need for corrections and laboratory tests to characterize sensitivity behavior against various conditions for species of interest.

Detailed comments:

Line 11, “Finally, we demonstrate the capability of the t-IMR...”, it would be useful to report sensitivity and LODs for HOBr, Br₂ and HNO₃ in the abstract. It would be even better to compare these LODs and sensitivities to the standard ‘low-pressure’ IMR design.

- We have added a table with LOD and sensitivity values for key compounds

Line 25, add CF₃O-, to this list, one of the major adduct ion chemistries.

- Added the mention

Line 31, maybe add the design impacts backgrounds as well, which doesn’t impact sensitivity or selectivity directly, but is important in instrument performance, and one of the benefits of the tIMR design.

- Added the mention of background signals to this statement

Line 46, “And of equal importance...”, I think the authors a referring to wall effects and effectively the importance of quantifying backgrounds in the instrument accurately? As worded it is a little unclear with the authors mean.

- We combined sentences and changed wording here to be more clear. What we mean is that the goal is to disturb and change analyte molecules as little as possible to ensure measurements effectively capture ambient composition, which does include wall effects.

Line 88, “Teflon™...” is this FEP or PFA?

- PFA, and we now say so in the manuscript

Line 100, “via a gaseous mix...” Please specify mixing ratios and flowrates of MeI and toluene

- We do not have exact mixing ratios measured to report, but we have moved up the statement about flow rates and conditions under which reagent flows are generated

Line 112, “The orifice, highlighted in purple in the inset, is designed specifically to maintain the pressure difference between the IMR at a somewhat dynamic atmospheric pressure on the order of ~1000 mbar and SSQ operating at 2 mbar.” Does the orifice change diameter? How does it maintain a pressure difference between the IMR and SSQ? Is the pressure in the tIMR monitored continuously?

- We’ve changed the wording and specified in the text that the orifice diameter does not change, but was chosen to keep the SSQ pressure near 2 mbar when the IMR operates at atmospheric pressures (on the order of 1000 mbar)

Line 116, “...to provide a small concentric flow of UHP nitrogen...” how much flow is this, how is it controlled?

- We have specified the flow rate of 200 sccm (via an Alicat mass flow controller) in the text

Line 166, “d is the diameter of the IMR tube (m).” One could consider the characteristic length in the Re calculation as the IMR pipe length rather than the diameter. The authors should also calculate Re this way to ensure the system is laminar.

- The IMR pipe length is much larger than the diameter, when using this value as the characteristic length instead, the Reynolds number reduces to $Re = 24$. So we take the larger of the two in the text, which is still well under the values of 2000 required for a laminar flow regime.

Line 197, “Here, between 12 and 14 LPM of nitrogen is introduced...” so does this mean backgrounds are determined dry? How do the authors correct for analyte sensitivity differences between dry and wet IMR conditions? How long and often are backgrounds determined?

- Background determinations are dry, backgrounds were attempted almost twice daily in the field using an automatic delivery system which proved to be problematic, so 5 manual robust background periods are used for BLEACH data. Water vapor dependent sensitivities are applied to the key compounds for which we have experimentally determined relationships (see below comment and new appendix section on PH₂O dependence)

Line 203, “Low pressures...” This sentence and the following seem out of place in the paragraph.

- We agree, and moved this section

Line 223, “Br₂I⁻ cluster peak...”, which one?

- m/Q 284.74, constrained isotopically at the m+2 and m+4 values, now mentioned in the manuscript

Line 229, “However, maximizing kinetic energy...” There is this effect but could the increase in field strength also simply be de-clustering the product clusters?

- That is also possible, and is now included in the text

Line 258, “To characterize our t-IMR...” this section should be moved to a separate section in the Methods.

- To preserve the logical flow of the paper from IMR description to the individual demonstrations of abilities and improvements, we've chosen to leave the brief details of experimental setups at the beginning of each section

Line 285, “...especially after accounting for the t-IMR residence time of 0.75s” Could you include the Palm et al. low pressure IMR residence time as a comparison point here? My understanding is this was on the order of 50 - 100 ms?

- What was meant here is that the 1-2 second delay is made even less significant when subtracting the residence time of 0.75 s, not that our residence time is shorter than Palm's, which appears to be 100 ms based on a brief mention in their paper. We've deleted the phrase involving 0.75 s to avoid confusion.

Line 286, “This result is also comparable...” did the authors also do this experiment for HNO₃? It would be a nice comparison to the Zhao et al. 2017 paper result.

- We have performed this experiment after submission and added the results to the appendix (and a mention in the corresponding section)

Line 290, “The t-IMR was deployed...” much of this section could be moved to the Methods section as a “Field Deployment” section.

- See previous comment re: flow of article and methods

Line 306, “LOD is also calculated...” Please include a table of these LODs and for what integration time.

- Now included in a table with LOD and sensitivity

Line 315, “binding enthalpies...” Please move these DFT methods to a separate methods section.

- See previous comment re: flow of article and methods

Line 326, where did this equation come from? Was a water dependence of the Br₂ or HOBr sensitivity considered?

- An explanation is added for the equation and experiments were conducted on water dependence after manuscript prep, results have now been added here. We've added an appendix (B) showing a water-vapor dependent curve of Br₂ and HNO₃ sensitivity based on both in-field calibrations and laboratory experiments. The HOBr and HNO₃ timeseries and diurnal profiles have been updated to reflect this dynamic sensitivity, which does not change the behavior of either significantly, nor the conclusions of this work.

Line 330, “The daily maximum levels of HOBr...” It would be useful to include Br₂ and BrO data in this figure and analysis to confirm this measurement. Additionally, isotopologue ratios is normal practice when reporting halogens and should be included in the SI.

- The high resolution spectra are shown in the appendix to confirm the isotope ratio of the identified HOBr peak fit. Br₂ and BrO data are included a forthcoming comprehensive Br observations manuscript. We aim here to demonstrate the deployment ability of the t-IMR and low LODs, and would like to save potential discussion of observed bromine chemistry.

Line 336, “However, in this case, the signals are converted to atmospheric concentrations using a direct calibration of the t-IMR after the campaign.” It is not clear why this was done rather than using the same approach as HOBr. Please show the equivalent result with the BE scaling approach. What was the sensitivity for HNO₃? How was the water dependence of HNO₃ sensitivity determined and applied?

- We now use the BE method for HNO₃ sensitivity and have applied the above mentioned water vapor correction

Line 351, “However, there are periods during the night...” The iodide CIMS measures N_2O_5 and HPMTF very sensitively, if either of these chemistries are at play the authors have data to prove this. Please include this or remove the speculative statement.

- We have now added and referred to a figure in the appendix showing N_2O_5 as well as ClNO_2 signals increasing with HNO_3 and NO_2 overnight to support this statement