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Comment on amt-2021-57

Anonymous Referee #2

Referee comment on "Iodide CIMS and m/z 62: the detection of HNO_3 as NO_3^- in the presence of PAN, peroxyacetic acid and ozone" by Raphael Dörich et al., Atmos. Meas. Tech. Discuss., <https://doi.org/10.5194/amt-2021-57-RC2>, 2021

Review of "Iodide-CIMS and m/z 62: The detection of HNO_3 as NO_3^- in the presence of PAN, peracetic acid and O_3 ", amt-2021-57

This is a very nice manuscript that explores a large dynamic signal that occurs at mass to charge ratio 62 (NO_3^-) in the iodide CIMS instruments. This signal has long puzzled users of the iodide ion for detection of trace gases, and this manuscript adds extremely valuable information to that ongoing debate. The manuscript is clearly written and organized and presents a well thought out convincing argument assigning signal at 62 to HNO_3 detection via the IO_x^- anion. This will be a valuable addition to the existing literature on iodide CIMS and I fully support its publication pending minor changes.

It has been my own experience, having run a similar set of experiments, that addition of significant O_3 to the iodide CIMS instrument while holding HNO_3 addition constant will result in observable depletion of IHNO_3^- observed at m/z 190, even when normalizing to iodide. The authors convey nicely that the impact of ozone on signal detection will be highly variable depending on the instrumental conditions used, and that alone could be the difference here. However, considering the authors present HNO_3 data from the field using observations at m/z 190, the data should exist from the laboratory experiments to validate that this does not occur in their system. It would be beneficial to this manuscript if the authors could include a figure similar to 7a but looking at the signal at m/z 190. This information is important to validate some of the assumption throughout the manuscript such as on page 8, line 232 where it is indicated that "negligible depletion of HNO_3 " occurs, a fully testable assumption considering the ability to detect HNO_3 at m/z 190. It would also be useful in understanding the comparisons of the m/z 62 and m/z 190 data at the end of the manuscript from the ambient observations.

I am having a difficult time understanding how the authors are able to retrieve an ambient HNO_3 signal from the NO_3^- signal. The signal that occurs at that mass is dependent on a changing HNO_3 ambient concentration as well as a changing O_3 concentrations. It would seem rather difficult to retrieve the real concentration unless you make an assumption that at any given point HNO_3 is not changing and only O_3 is changing, or the other way

around. The only way this may work is if the authors used a measurement of true O₃ collected during the ambient flights, however it is unclear from the description that this was the case, perhaps those details are just missing. If an ozone measurement was used what instrument provided that data. I would like to see more details of how the concentration profiles in Figures 9 and 10 are determined, and what assumptions were made. If the author agree that one can not retrieve true HNO₃ unless a true ozone measurement is used it would benefit the readers to explicitly state this. It is possible that a reader could interpret the data presented here to mean that by using the Iodide CIMS measure of IO_x⁻ and NO₃⁻ one can quantitatively measure HNO₃.

I am in general surprised by the lack of instrument response to ambient features in the data in figures 9, 10 and S1. HNO₃ should have a significant inlet response time relative to O₃ in the CIMS regardless of the inlet conditions. In figure S1 in particular there appears to not be any lag in the observations. This quality in addition to the exact correlation to O₃ makes me believe that you are really just detecting HNO₃ that is made inside of the instrument. Otherwise, I would expect some deviation between the ambient O₃ and HNO₃ from 12:00 to 15:00 in figure S1. Can the authors comment on the time response of their measurements? What does a laboratory time response on m190 look like relative to m62?

Has the data from Figure 10b been corrected for scrubber zeros? Is this actually signal over zero. The way the data correction is explained for 9b where an approximate exponential of the Po HNO₃ source is subtracted out would suggest that there are not real zeros removed from the ambient data, which would include source HNO₃. If real zeros have not been used how do you know any of the features shown in figure 9b or 10b are real ambient signals. If real zeros were used why didn't they account for the Po source background?

This ion chemistry is ultimately a three-body reaction as indicated in page 7, line 216. Therefore, the result should be quite dependent on IMR pressure. The iodide CIMS literature is filled with instruments running across a very large range of pressures, sometimes exceeding 100 mbar, do the authors have any data or comments on the impact of pressure on this ionization mechanism.

The authors comment on the potential issues with past data sets using iodide CIMS to measure PAN, due to the secondary acetate ion chemistry that is occurring. It is my experience that many if not all of the airborne systems employ a constant standard addition of ¹³C PAN to the instrument. I believe that this addition would account for any secondary ion loss due to IO_x⁻ chemistry. I think the authors should add a comment in their discussion on this point on pages 9/10. While there are likely many dataset that have not used such an internal standard to track sensitivity changes it is not appropriate to question the data set that have used that method. A related question is do the authors believe such a system would indeed correct for these ion chemistry issues? That could be a good couple sentence discussion to add here.

On page 12, line 369 the authors state that 190 does not show any correlation with O₃. However, in the same figure, #10, it is clear that 190 correlates with m62. It was previously argued in describing figure 9, using panel C that it is expected that HNO₃ should correlate with O₃ even after correction for this unique ion chemistry. Additionally, there are clearly features in 10b that correlate with the ozone signal shown in 10a. Please elaborate on the disagreement between these two statements.

On page 6 there is a discussion on the residence time in the flow tube and comparison to similar work. I encourage the authors to reconsider their calculation of the residence time in their flow tube as presented. With a critical orifice on a cylinder there will be a jetting effect of the air through the region such that your reaction timescale will not be equivalent to the laminar sweeping of the volume. Rather it will be dependent on the velocity and flow dynamics of that jetting effect. This likely results in a significantly shorter reaction time than the volumetric calculation for most of the analyte molecules being sampled. It is not necessarily a discussion that is needed here but should be considered when trying to understand the difference being discussed, and leveraged as a potential answer for some of the disagreement observed.

Figure 1. I am interested in the flow dynamics in the figure with the initial sampling line. It appears that at some point your inlet could be connected to a pump exhaust line in the far left of the diagram. Even if overflowing the inlet with N₂, depending on the flow characteristics and pressures I could see a scenario where pump exhaust would flow out the inlet past your sampling point. Perhaps something is missing or I am interpreting this diagram incorrectly.

Why do the authors believe the HNO₃ to 62 appears nonlinear in the inset figures on Fig 2 and 8?

Figure 9 and 10. These figures are difficult to interpret because there is not legend given in the figure and the colors are reused for different species. In 9, I believe the label attitude should be black and without reading the caption the reader has no idea what the pink line is for example. Blue is used in 3 places in Fig 9 for three different things.

Page 8, line 238 needs a space between the and IOx

Page ,8, line 241, suggest adding the word "of" in front of 100 greater.

Page 9, line 265, there is a close parenthesis missing.

Page 12, line 371, calibrations should be singular