



EGUsphere, referee comment RC1
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Comment on amt-2022-295

Anonymous Referee #1

Referee comment on "Temperature-dependent sensitivity of iodide chemical ionization mass spectrometers" by Michael A. Robinson et al., EGU sphere,
<https://doi.org/10.5194/amt-2022-295-RC1>, 2022

This paper, *Temperature dependent sensitivity of iodide chemical ionization mass spectrometers*, describes observations of instrument performance made during laboratory experiments and previous field campaigns to understand unexpected instrumental behavior. Iodide Chemical Ionization Mass Spectrometers (I-CIMS) are used by numerous groups worldwide to measure a variety of species including halogens, NO₂ constituents and oxidized organic compounds. This makes this paper highly relevant to the community. On its face, it seems obvious that higher temperatures would result in less strongly bound clusters falling apart but it is not something you typically see considered in these types of measurements. Since cluster chemistry is important to other ionization schemes beyond iodide, the significance of this work extends to other ion chemistries as well (eg. NH₄⁺, Br⁻, Fluoride transfer). One part I feel should be made clearer is which experiments were done with which IMR. I realize the IMR heating experiments were performed with the Aerodyne IMR, but what about the cooling experiments or the room temperature sweep experiments? This is not clear to me and left me confused as to which IMR was used where. I suspect I would not be the only one. I am wondering if the authors could also provide a few more details about the closed loop humidity control. This should be added to the SI. It would give the reader a better understanding of how this system works and the variability of the amount of humidified nitrogen added. Since the I(H₂O)⁻ cluster is both a product ion and also a reagent ion the temperature dependence of it has important direct and indirect implications on the instrument sensitivity. The manuscript is well written and falls within the scope of AMT. It should be published once the few minor comments are addressed.

Specific Comments

P1 L 23: Sentence should be reworded. It gives the reader the impression that only cooling reduces the sensitivity drift.

P1 L26: Atmospheric trace....

P3 L73: This is a very good point. I am struggling to think any temperature dependent studies beyond some of the initial kinetics papers in 90's.

P4 L103: The authors should provide a couple of example analytes not merely the reference.

P4 L114: The stabilization of sensitivity assumes the clusters make it the detector without falling apart, also dependent on the operating pressure of SSQ there is potential for chemistry to continue into this region which is never temperature controlled on any of these instruments.

P5 Figure 1: It seems odd to me that the nylon liner on the NOAA IMR does not provide some form of temperature isolation from the outside temperature of the stainless steel fittings. Clearly, it's just not enough isolation

P5 L131: How much N₂ do you have to flow through the bubbler? Is it the same flow to maintain the same cluster I⁻:I(H₂O)⁻ cluster distribution in the two IMR's? I am curious because dependent on IMR geometry I have seen this vary greatly in our instrument.

P5 L 138: I'm curious why the authors chose only to normalize by the $I(\text{H}_2\text{O})^-$ cluster. Granted it should account for any variation in reagent signal it is merely that often in the literature the reagent is taken as the sum of the two.

P6 L157: From the looks of the temperature profile these experiments, they were not done as ramp and soak type experiments. I'm curious as why this decision was made as opposed to trying to assess the issue at discrete temperatures. Granted this mimics what typically occurs in most measurement trailers or aircraft.

P7 L172: Do you have any idea as to the actual gas temperature in the IMR's? I am guessing even with heating or cooling they would be very different when the instrument is operated as a PAN CIMS.

P7 L179: are shown

P8 Table 1: I am curious why you did not calculate the sensitivities for 2-nitrophenol and phenol if you know what mixing ratio added to the inlet is?

P8 L204: It is not exactly fair to compare the PAN chemistry (particularly the anion chemistry) when the ionization chemistry is a different mechanism than the rest. The authors should specify which channel or drop it and merely discuss the halogens.

P9 L212: Again, I am not sure grouping the PAN anion channel with the others is appropriate.

P9 L215: Why were the sensitivities not determined?

P9 L227: How much nitrogen needs to be added/removed for the humidity control? Are we talking about 10's of sscm on a couple of litres or is it more? I am curious if there is any possibility of dilution in the IMR and without that information, it is not clear to the reader.

P10 L230: $I(H_2O)^-$ is also a reagent ion. If it is falling apart in the IMR as a result of increasing temperature that would have a direct effect on sensitivity beyond clusters falling apart downstream.

P12 L280: This is definitely true.

P12 L283: At what pressure do you operate the NOAA I-CIMS SSQ? 2 mBar or lower?

P13 L294: Are the sensitivities the same using both NOAA IMR and the Aerodyne one?
There are definitely geometry differences between the two. Were the cooling experiments only done with the NOAA IMR and heating experiments only done with the Aerodyne IMR?