



EGUsphere, referee comment RC2
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Comment on amt-2022-295

Anonymous Referee #2

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-RC2>, 2022

This publication details a set of laboratory experiments examining the effect of temperature on a chemical ionization reactor employing the iodide anion as a reagent. The experimental results are then used to correct a field data set for ambient temperature variations.

In some ways this is an unusual manuscript. It contains information that typically would comprise the SI of a paper detailing the results of the ambient measurements. But I think that hiding many of these experimental instrumental details in the SI has previously been a disservice to the community. SI sections are rarely read nor widely disseminated, and such important details should be out in the open as these instruments proliferate across atmospheric chemistry.

However, this manuscript should be more clearly written and organized than it currently is.

I support publication eventually after the authors address the items listed below. More experiments should not be necessary, but I suggest major rewrites for clarity. Additionally, there are several places that the authors speculate about instrumental details and results without supporting evidence. These should be clarified with much more precise language.

Specific Comments

L87: "This discrepancy..." The authors should add proof of this speculation via a citation or data.

L95: The connection between this work and Lopez-Hilfiker's voltage scanning method is not clear to me, nor is the reason for this paragraph.

L108: Typically the last paragraph of the introduction focuses on what the forthcoming paper has done. Instead, this manuscript introduces another paragraph referencing previous temperature control strategies. This paragraph is disorienting. It should be moved to earlier in the introduction or later in the results. Also, the authors reference the FIGAERO as an IMR temperature control strategy, which is incorrect. The FIGAERO is an inlet that goes on the front of the IMR and is independent of the IMR itself, separate from the IMR's temperature regulation or lack thereof.

L117: My understanding of the Tofwerk instrument is that it is an OEM instrument, onto which others can install ionization sources. So this would seem to not be a "modified commercially available TOF", which the authors directly contradict anyway in L123 where they say the "TOF has not been modified."

L120 seems to refer to the IMR, but these running conditions in Lee et al. are specific to Iodide and Bertram et al. used pressures of 20-100 mbar. This entire paragraph should be edited for clarity.

L121 "It is worth noting that higher pressure IMR systems will likely be more susceptible to thermal effects due to the increased residence time" certainly seems possible but is still speculative and should be supported in some way.

L140 I was surprised here to read that this work also uses the ARI IMR since the entire introduction focuses on the NOAA-built ionization source. There is no prior introduction to the ARI IMR and no discussion on its specifics, nor a citation where it's referenced here. I suggest adding more detail on the ARI IMR to the main methods section (more than just the tiny table in the SI). Further, regarding the L117 comment, is the NOAA instrument any different than the commercially modified one if it sometimes employs the ARI IMR?

Section 2.1: The authors start this paragraph off making a claim that a constant IMR but a changing TOF temperature would cause temperature-dependent ion chemistry in focusing ion optics. But it doesn't appear that the authors conducted this experiment. Could they please support this claim?

Supplemental figures 1 and 2 should be cleaned up and moved to the main paper as a multi-panel figure referenced in Sections 2.2 and 2.3. This is a short paper and its entire value is that it is not hidden in the SI (see general comment above).

L239: The text references slopes on the graph, which I think is a good idea, but there are no slopes. The authors should add slopes to Figure 3, or if too busy, add a plot with an example regression. I find section 3.2 to be the most interesting, but it is short on details and specifics.

L258: I'm skeptical that HCl "fall[s] close to the 1:1 line". It has essentially the same measured reaction enthalpy as Phenol and HCN within the margin of error, but a different literature enthalpies. Is this a small influence of ligand switching? Why does nitrophenol fall so far off the line and is not discussed other than having a low overall sensitivity? This section could benefit from more analysis and textual interpretation.

L277: These field temperature swing would be a useful SI figure and the authors should have plenty of good examples.

L308: "Temperature control of the IMR region can help reduce the impact, but de-clustering can occur further in the instrument ion optics." The link between collisional fragmentation and temperature dependence is not clear to me as this is written.

All over: sensitivities in units of Hertz or ions/s should be defined with an extraction frequency for the TOF.

Technical Comments

L99: I'm not sure I follow the sentence at L99. Please clarify or add more detail: "Additionally, product ion formation dependence on temperature may make these voltage scanning determinations difficult to interpret"

L51: "refined restriction policy" – This could be clearer

L241: The nist webbook should be a citation in common citation format

L299: "dependence of sensitivity on temperature"