Comment on amt-2021-164
Anonymous Referee #2

Referee comment on "Quantification of Isomer-Resolved Iodide CIMS Sensitivity and Uncertainty Using a Voltage Scanning Approach" by Chenyang Bi et al., Atmos. Meas. Tech. Discuss., https://doi.org/10.5194/amt-2021-164-RC2, 2021

Review of “Quantification of Isomer-Resolved Iodide CIMS Sensitivity and Uncertainty Using a Voltage Scanning Approach”

AMT 2021-164
Bi et al.

Summary:

Organic aerosol reaction products from limonene+O3 and trimethylbenzene+OH were measured using a custom thermal-desorption GC instrument with the GC eluant split between an FID and a chemical ionization mass spectrometer using I- CI. The purpose was to understand the accuracy of the so-called “voltage scanning” method of I- CIMS calibration, in which collision-induced dissociation is used to quantify the ion-molecule adduct binding energy, which supposedly is linearly correlated with sensitivity. The assessment was done by comparing the voltage scan parameter dv50 to sensitivity determined by a combination of FID and chemical formula (from CIMS). The findings are that sensitivities vary greatly between isomers; dv50 is a poor predictor of sensitivity for individual compounds, but may have some use when many compounds are summed; and GC retention time has limited relationship with sensitivity.

Major comments:

The manuscript is well-written and well-organized with a nice attention to detail. The subject matter is certainly worthy of publication, since it addresses a useful and somewhat controversial question in the CIMS community. Many of my questions on a first reading were answered later in the manuscript.

I have one major issue with this manuscript, and several overall questions:
Major issue: From Figure 4, it really does not look like the voltage scanning method works especially well. It looks slightly better if some averaging is done (Figure 5, although I have some reservations about the mathematical appropriateness of the average -see below). However, it is hardly useful for individual compounds. This is surprising since the theory seems solid, and previous work indicated that there was certainly a relationship between the voltage scan parameter and sensitivity. What is missing from this manuscript is some discussion of why the experimental relationship is so weak. The experiment was designed well, but are there some experimental uncertainties that could explain the results? Or is the theory "wrong" – meaning that dv50 does not correlate with binding energy, and/or binding energy does not correlate with sensitivity for some compounds? If so, why? Even some speculation in the discussions section would be useful, since it could provide some ideas for how to improve the method.

Overall questions:

1. The voltage difference between the skimmer and the BSQ affects not only the molecule-adduct declustering environment, but also the transmission efficiency of ions into the BSQ. Do you have a sense of the relative magnitude of these effects? Could it be important to normalize to some metric of transmission efficiency? Additionally, in lines 143-145, it seems you are normalizing to the reagent ion signal, but this also changes during the voltage scan. Could this distort the shapes of the sigmoid curves, since you are not measuring directly the change in signal, but rather the change in signal relative to the change in I- signal (or sum of I- and IH2O-, not sure which was used here)?

- Second, I have some related questions about the accuracy and precision of this method. a) How sensitive is this method to instrumental noise? Or, in other words, what signal-to-noise ratio in the actual measurement is required to achieve meaningful results? b) How sensitive is this method to the quality of the sigmoid fit? What is the typical uncertainty in the fit parameters, and how does this translate to uncertainty in the calculated sensitivity? c) How sensitive is this method to instrument settings? The chosen setting of V0 – the baseline skimmer-BSQ voltage – is probably quite important. Are there other instrument settings (pressures, voltages) that need to be exactly right for this method to work?

- From figure 2 (and text) it is clear that many isomers may exist in chamber experiments (and also in ambient samples). What happens to the voltage scanning results when two or more isomers, with differing sensitivities, are present? Is this discernable in the shape of the sigmoid curve? At line 390 you state that the functional dv50 of an isomer mixture is equal to a signal-weighted average of the dv50 of each individual compound, but looking at the formula for a sigmoid function, it’s not obvious to me how this is true. Can you show that the experimentally-fit dv50 of a mixture is equal to the weighted average of the individual species, especially when the baseline signal is different for each compound and unknown for a mixture?
Is it even possible to use this quantification method when air is sampled directly, without pre-separation? And, from Figure 2, it seems the chromatographic peaks were not well-resolved, even for a single CI formula. If the chromatographic peaks overlap heavily, sensitivities vary greatly between isomers, and you are only able to accomplish one voltage scan per chromatographic peak, is this not problematic? How did you address this issue?

Finally, having used I- CIMS for many years, I am curious about the identities of the non-iodide-adduct ions (i.e. the usually open-shell ion formulas without iodide). This experiment might be an avenue to say something comprehensive about how to interpret these ions. Did you look into these measurements? I understand this is probably outside the scope of this particular manuscript, but would like to know if you have any observations or plans to investigate this topic.

Specific/minor comments:

Lines 140-151 (CIMS configuration):

The pressure, humidity, reagent flow, and voltage configuration (in standard operating condition) of the CIMS should be restated here, since other I- CIMS operators will likely use this paper as a guide for configuring their own instrumentation.

Lines 170-185:

The discussion of timing here is confusing. If I understand correctly, the difficulty lies in measuring quickly enough to capture the elution of a single chromatographic peak. What is this timescale and what is the actual measurement speed required? Additionally I don’t understand the reasoning behind measuring every 50ms and then averaging three data points. Why not record a measurement every 150 ms?

I think Figure 1 would be improved by showing a time-series of the voltage settings, rather than the blue numbers.

Lines 193-196:

Wouldn’t it make more sense to normalize to the maximum signal, rather than the signal at the arbitrary base voltage = 2? Presumably there are some compounds that do not experience the maximum signal at V=2, but rather at lower voltages.

Lines 268-270:

This approach could possibly bias your results against compounds with particularly low CIMS sensitivity (where the CIMS peak was too small to meet your section
criteria) or with particularly high CIMS sensitivity (where the FID peak did not meet the
criteria). Were there many peaks that were rejected, and were they mostly CIMS peaks or
FID peaks?

Figure 3:

It isn’t clear whether this figure shows the absolute distribution of sensitivities,
or the distribution scaled by the signal abundance of each isomer.

Figure 4:

I don’t think it is very useful to size the markers by the molar abundance, since
there are four distinct experiments shown here, and it is not very meaningful to compare
the molar abundance of specific compounds between different experiments (and especially
not between the oxidation experiments and the liquid standards).

Lines 377-380:

Are there any unifying features of the compounds with lower sensitivities? At
line 385 you state they are less sensitive compounds, so they may be overwhelmed by the
stronger signal from more sensitive compounds. I don’t understand this – do they actually
have lower sensitivity, or is this just an artifact? And was not the point of the GC pre-
separation to be able to consider high-sensitivity and low-sensitivity isomers separately?
Additionally, I think it is somewhat misleading to call these “outliers” when they comprise
a quarter of the overall dataset.

Lines 425-434:

Assigning sensitivities randomly distributed around a mean also does not
introduce significant bias overall, so I don’t think this says much. Could you not achieve
the same result simply by calibrating a single compound known to have average
sensitivity, and applying that single calibration factor to all compounds?