

Atmos. Meas. Tech. Discuss., referee comment RC1
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Comment on amt-2021-149

Anonymous Referee #1

Referee comment on "Correcting bias in log-linear instrument calibrations in the context of chemical ionization mass spectrometry" by Chenyang Bi et al., Atmos. Meas. Tech. Discuss., <https://doi.org/10.5194/amt-2021-149-RC1>, 2021

This manuscript presents a method for addressing a common source of bias that affects a common calibration method relevant to the measurement of trace gases in the atmosphere. This bias arises from the use of regressions in log-linear space without accounting for how the log-transformation impacts the distributions of uncertainty in calculated ion sensitivities. The manuscript is well-written and suitable for publication in AMT following some minor revisions.

It took me a little too long to figure out that in Fig.1 the authors were using a pre-determined fit and sigma to simulate the sensitivities of 100 ions. The default interpretation of these figures is that the plotted line is a fit of the synthetic data, which is exactly backwards in this case. I think a little clarification in the figure caption (and maybe the text) on how the authors simulated the dataset in Fig. 1 would help readers avoid this confusion. Alternatively, Fig. 1 might be more intuitively presented by showing the probability distribution of sensitivities surrounding the assumed fit as shading, rather than through a synthetic dataset plotted as markers (which are too sparse to really see the distribution, unlike e.g. those in Fig S5).

The implicit assumption in this analysis is that the error in sensitivity is normally distributed for all calibrants. Given what we know about the challenges in calibrating sticky molecules, is there a risk that the distribution of errors in a calibration set are not normal, and are actually skewed away from $\epsilon=0$? Since the number of calibrants included in the regression of S vs dV50 is typically very low, it seems like there is significant potential for one or two biased calibrants to shift the S vs dV50 relationship by an amount that is greater than the correction outlined in this manuscript. I would like to stress that this question does not take away from the usefulness of the authors' technique.

I am also wondering about the fundamental relationship between binding enthalpy and CIMS sensitivity and whether or not the set of compounds that are easily synthesizable (commercially available) are representative of those that are not. That is to say, the same

aspects of chemical structure that make a compound challenging to synthesize (many different functional groups on the same carbon backbone) are also the things that determine how efficiently a molecule can bind to a reagent ion. This is certainly a question beyond the scope of this work, but I think a brief discussion of this weakness in the application of voltage scanning to analytes with unknown structure would fit in well with the parts of this manuscript that discuss what the relationship between S and dV_{50} means (line 172).

58: There is a step missing between what is shown in Lopez-Hilfiker et al 2016 (dV_{50} is an indicator of binding enthalpy) and the authors' conclusion that sensitivity and dV_{50} have a log-linear relationship. I think an additional citation to Iyer et al. 2016 is warranted here.

115: The phrase "analyte-reagent ion binding-enthalpy" was confusing to read because of all the hyphens. I would reword this to "the binding enthalpy of the analyte with the reagent ion" or similar.

224: Framing slope as a negative value has flipped the reader around from what is plotted in Fig. 4. I follow the authors' reasoning and the math, and I think that readers would follow along more easily if the authors did some combination of 1) including ΔdV_{50} as a second x-axis in Fig. 4 2) explicitly address at ~line 224 that the use of ΔdV_{50} has changed the sign of the slope compared to when it is plotted against dV_{50}

330: Just I-CIMS calibrated through voltage scanning, not I-CIMS in general.

Fig. S5: This figure is helpful for seeing the interplay between the shape of the voltage scanning dataset and the bias introduced at different dV_{50} . I found myself wanting to know the average % bias in the measured mass of analytes for the No-Correction fit in each case. It's another number on a very full figure, but I think it'd be worth it.