Dear Editor,

We thank the reviewers for taking the time to review our manuscript and for their valuable feedback. We have carefully considered their suggestions and made the necessary revisions to enhance the clarity and accuracy of the manuscript. Below, we provide a detailed response to each of their comments. For your convenience, we have marked the reviewer comments in blue, our responses in black and parts of the text reflecting changes in the manuscript in purple. Please note that the line numbers in our responses correspond to the manuscript with tracked changes. Thank you once again for the feedback.

Reply to Reviewer 1:

This manuscript presents sensitivity estimates for Br- and I- CIMS using the voltage scanning method. It follows several earlier studies where this approach has been utilized, and it is likely a useful addition to the growing literature on the subject. I recommend publication after revisions, and list my main comments and concerns below, with the major one relating to lack of novelty.

We appreciate the valuable feedback from Reviewer 1 and provide the response to each of comments in the following.

General comment

Comment1: It is not very clear to what the novelty in this specific work is. Lopez-Hilfiker et al. presented a very similar set of results for I- CIMS in 2016, and there have been several other papers following up with additional details after that. I started reading this manuscript with high hopes for some new insight, methodologies, or guidelines. In particular as the title said "From Signal to Sensitivity", suggesting that the manuscript would contain new and in-depth methodology. However, now I have to suggest to the authors to more clearly showcase what this manuscript presents that is actually new in the context of "Atmospheric Measurement Techniques". The authors themselves note in the introduction that "voltage scanning is one of the most frequently used semi-quantitative calibration methods".

This is my only general comment, since in general the manuscript reads well and is quite straightforward, but this is partly because the authors are following similar steps as earlier studies.

Reply1. We thank the reviewer for this comment. The aim of this study is to demonstrate how voltage scanning can be implemented in the newly developed Vocus AIM IMR, which is grounded and operates at a fixed potential. In addition, it provides theoretical and experimental insight into how different functional groups influence molecular sensitivity in Br-CIMS and I-CIMS.

In the revised manuscript, we present an expanded discussion on the necessity of implementing the voltage bias in Vocus AIM IMR and how this bias enables accurate voltage scanning results. The method is further applied to our Vocus CI-TOF, demonstrating that it is broadly applicable across instruments employing grounded IMR designs.

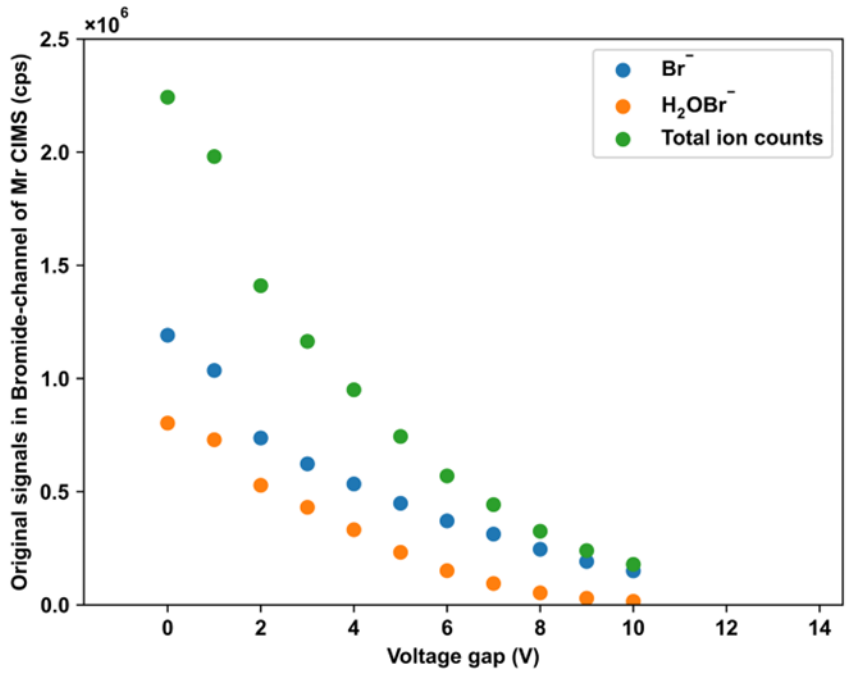
We revised Page 5, Line 10 to Page 6, Line 6 as: 'The Vocus AIM IMR is configured to be electrically grounded, which differs from earlier CIMS designs (Lopez-Hilfiker et al., 2016). For anions, an increase in the voltage gap between SQ and BSQ will lower the potential of SQ relative to the grounded IMR and thus can generate a retarding electric field at the reactor exit. This will reflect ions back toward the IMR because anions are decelerated when moving toward regions of lower electric potential. A similar argument applies to cations in positive channels. This effect results in ion repulsion, i.e., reduced ion transmission, and can result in a decrease in ion signals. Consequently, the measured signal decay rate reflects not only the declustering

processes occurring after Skimmer, which indicates the cluster binding energy, but also variations in ion transmission across the IMR–SQ interface. Since voltage scanning is used to derive the cluster binding energy based on the signal decay, we have to minimize the above issue and ensure that signal decay rate is primarily determined by cluster binding energy.

Total ion counts (TIC) serve as a useful indicator of changes in ion transmission efficiency **(Figure S3)** (Lopez-Hilfiker et al., 2016). In this work a pinhole bias of −4 V in negative channels and +4 V in positive channels is implemented across the IMR–SQ interface, i.e., Reactor Back, at the start of scanning. This approach results in a fixed ion transmission offset from IMR to pinhole, but it ensures that the subsequent signal decay is dominated by variations in relative binding energies rather than by transmission artefacts from pinhole to SQ. This behavior arises because the strong gas expansion from IMR (~52 mbar) into SQ (~1.5 mbar) can efficiently drive the initial transport of ions, allowing anions to be transmitted with comparable efficiency from pinhole to SQ. It makes ion transmission relatively insensitive to variations in the SQ potential as long as the retarding electric field across the pinhole-SQ region remains moderate. Although ion transmission eventually decreases as the field becomes sufficiently strong, most clusters have already reached their dV_{50} by that stage.'

Figure S3 was added to help better understand the changes of transmission:

(a)



(b)

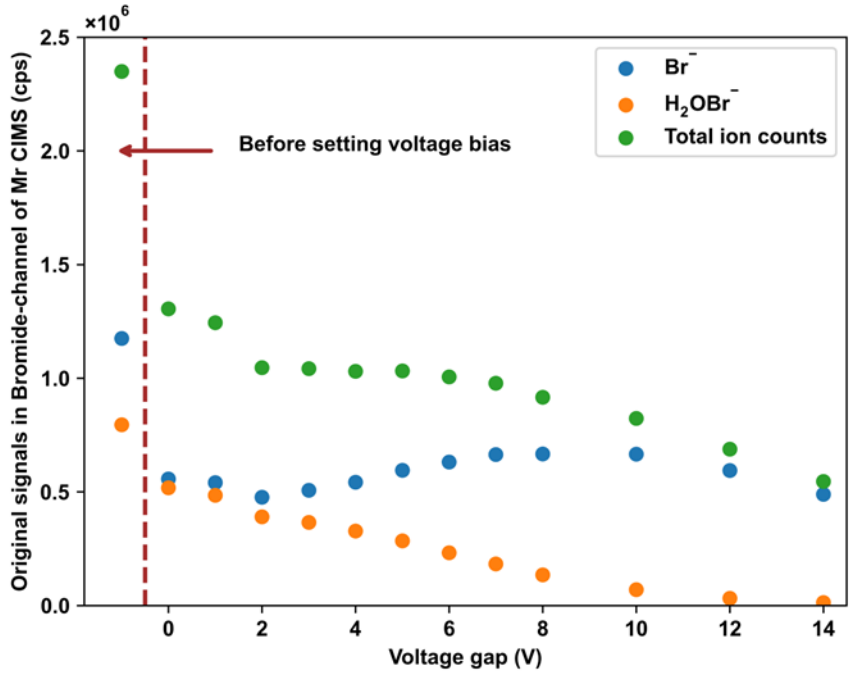


Figure S3. Signal variations of total ion counts (TIC), Br^- and H_2OBr^- (a) without a voltage bias and (b) with a voltage bias during the voltage scanning.

Specific comments

Comment2: Page 1, Line 17: How is the feasibility of the method actually shown? There is a figure with time series of different molecules, but those are not compared against anything else.

Reply2. The comparison with HONO is used to show the feasibility of this method and then applied to obtain the time series of the concentrations of these oxidation products. We revised Page 1, Line 16 – 17 as 'were taken as examples to show the results of this method for a daytime oxidation chamber experiment.'

Comment3: Page 2, Line 3: This reference seems limited concerning to generality of the sentence. Perhaps the authors could cite some recent review touching the subject, e.g. Zhang et al., 2023 (https://analyticalsciencejournals.onlinelibrary.wiley.com/doi/10.1002/mas.21857), or some CIMS comparison, e.g. Riva et al., 2019 (https://amt.copernicus.org/articles/12/2403/2019/).

Reply3. We revised Page 2, Line 4 as: 'It uses soft ionization to charge analytes and has the advantage of allowing in situ measurements that preserve the structure of the analytes (Riva et al., 2019; Zhang et al., 2023).'

Comment4: Page 3, lines 5-8. This is a key sentence of the manuscript, but it is now very long and hard to follow. I suggest splitting it in two and making it clearer. In addition, this paragraph is followed by two more, which read more as summaries and feel a bit misplaced at the end of an introduction.

Reply4. We revised Page 3, Line 6 – 11 as: 'Here we present an approach to estimating sensitivities of a wide range of compounds using multiple reagent ion chemistries in the grounded Vocus AIM IMR, whilst simultaneously tracking the collision limit sensitivity based on the method reported by Aggarwal et al. (2025). Based on this, sensitivities were for a wide range of species were obtained with this voltage scanning approach. We assessed the performance of this approach using a wide range of calibrants, chamber experiments and quantum chemical calculations.'

Comment5: Page 4, line 7: What does it mean that the VUC sources were switched?

Reply5. It means that the two VUV sources were alternately operated at a frequency of 1 Hz, with only one source active at any given time. We revised Page 4, Line 11 as: 'the two VUV sources were alternately operated at a frequency of 1 Hz to generate …'.

Comment6. Page 4, lines 8-9. Please add citation since you say it is well-known.

Reply6. We added the citations in the revised manuscript.
We revised Page 4, Line 13 as: 'on the sensitivity of CIMS (Huey, 2007; Lee et al., 2014).'

Comment7: Page 4, lines 18-21. I had to re-read these sentences several times and am still not sure I understood the details. Please try to make this more clear and easy to understand.

Reply7. We revised Page 4, Line 21 – 25 as: ''Data consist of four segments, each corresponding to a different reagent ion and were recorded with a time resolution of 0.5 Hz. For data processing, each segment was averaged by a factor of 2 and thus had an integration time of 1 s.

Comment8: Fig. 1, caption: I am used to seeing "SSQ", but is the first quadrupole not segmented in this instrument? In addition, quadrupole is misspelled in the figure.

Reply8. The first quadrupole in our Vocus B and Vocus CI-TOF is not segmented. Riva et al. reported that the optimal voltage gradients in the first quadrupole region are typically all 0 V between electrodes, as ions are focused on the radial direction efficiently by the RF but transported axially by the gas flow (Riva et al., 2024). Consequently, Tofwerk opts not to implement a segmented quadrupole.

Thank you for pointing out the spelling error. We have revised this figure according to reviewers' comments as:

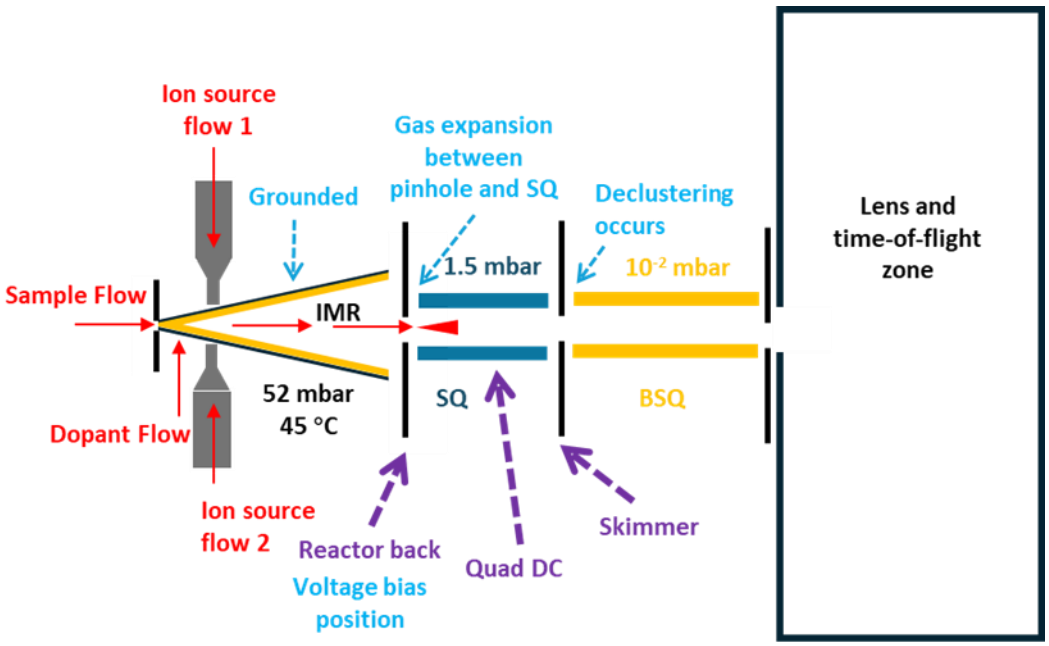


Figure 1. Schematic of the MR-CIMS structure. Gas flow paths are indicated in red, and key electrodes are highlighted by purple dashed arrows and texts. Explanatory annotations are denoted by blue dashed arrows and words. Pressures of the IMR, SQ (short quadrupole), and BSQ (big-segmented quadruple), as well as the temperature of the IMR, are labeled to facilitate understanding of the operating conditions in MR-CIMS.

Comment9: Page 5, line 4: Which are these "other voltages". The last mentioned one was the orifice plate, and if also all others were kept constant, then there would not be much changed at all? In addition, Table S1 provides voltages that were varied, but using nomenclature that is not used elsewhere, making it hard to relate to.

Reply9. We revised this section and give a detailed description and explanation for this voltage scanning method as well as its voltage bias setting. This can be found in Reply1.

We revised Page 4, Line 32 – 37 as: 'A schematic of the main elements of MR-CIMS including the IMR and quadrupoles, highlighting the region where the voltage was scanned, and the transfer of molecular ions to the TOF MS are shown in Figure 1. Three electrodes/voltages were adjusted in upstream of big-segmented quadruple (BSQ), including Reactor back, Quad DC, and Skimmer. Reactor back is the direct currency (DC) potential applied at pinhole between IMR and SQ, which is set as 0 V in the routine operation. Quad DC refers to the DC potential applied to the four quadrupole rods that carry the radio frequency (RF) field of SQ. Skimmer voltage corresponds to the DC potential applied to the skimmer electrode, which controls ion extraction and transmission efficiency across the SQ-BSQ interface. An increase in the voltage difference between the BSQ and region upstream of it induces dissociation of the adduct.'

Comment10: Page 6, line 12: KDE was applied to investigate the oxygen levels. How does KDE serve that particular purpose? And in the SI it says "We introduced it to ensure the completeness of the manuscript", which also confused me.

Reply10. KDE is principally a method to present the distributions of a finite sample of data. It overcomes the key limitations of traditional histograms, providing a better visualization of dV_{50}'s distribution. We revised Page 7, Line 15 – 16 as: 'Kernel density estimation (KDE) was applied to estimate the probability density functions of dV_{50} in both channels, in order to provide better visualization of the effects of …'

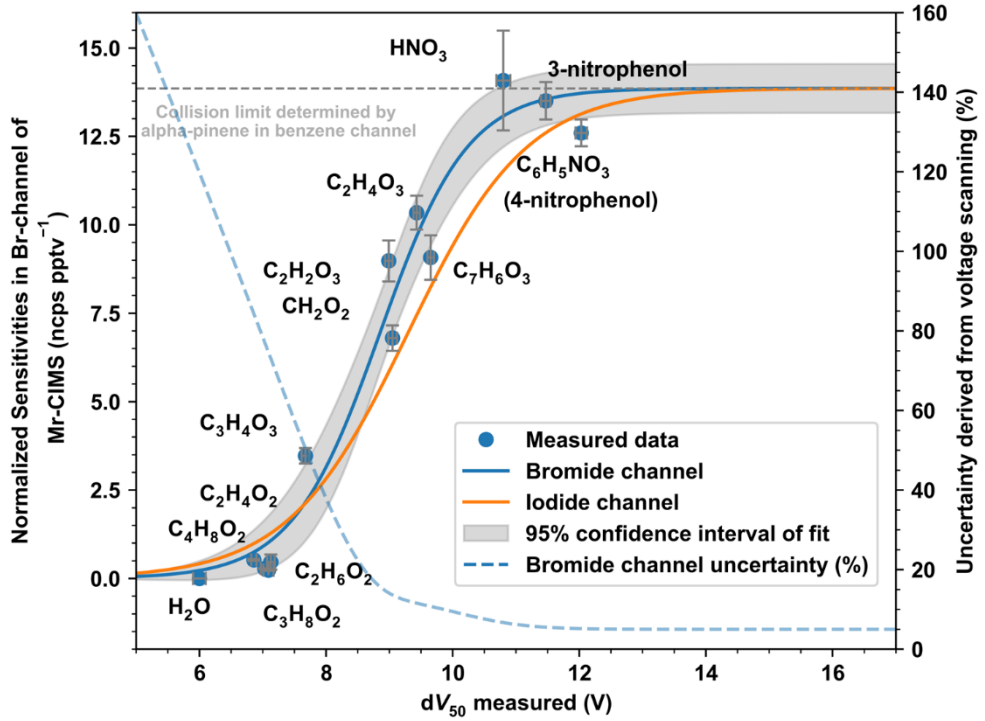
With respect to the latter query, this is probably a language misunderstanding. We revised the Section S1 in the supplement as 'We described it to ensure the completeness of the manuscript.'

Comment11: Figure 2: 1) The figures have two lines that refer to "uncertainty", and they are very different, and on different axes. 2) nitrophenol is misspelled in panel a. 3) Having the "I" in the formulas in panel b in the middle of the formulas, although they are adducts with I-, seems incorrect.

Reply11. 1) We already explained the uncertainty in the Page 7, Line 2 – 4 of original manuscript: 'The uncertainty in the estimation was defined as half the width of the 95% confidence interval of the sigmoid fit, divided by the corresponding fitted value, and was also treated as a systematic error associated with the use of this method.' The shadow indicates 'half the width of the 95% confidence interval of the sigmoid fit'. The right axis is the systematic error, which is the sum of squares of 5% uncertainty from collision limit determination and the standard error of sigmoid fit divided by the corresponding fitted value. This is further explained this in the revised version. 2) Revised. 3) We followed the ion formulas detected by mass spectrometer. To avoid misunderstanding, we only labelled formulas of analytes in the revised version.

We revised Figure 2 as:

(a)



(b)

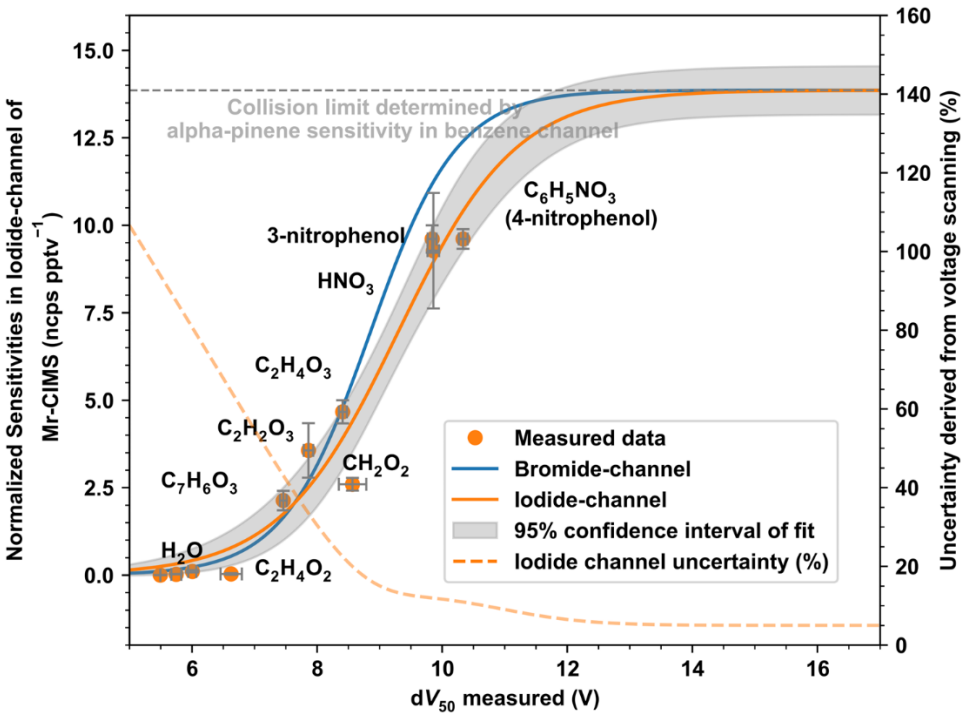


Figure 2. Relationships between dV_{50} of adducts and sensitivities to the corresponding species in the (a) bromide channel and (b) iodide channel of MR-CIMS. Fitting curves and 95% confidence intervals of dV_{50} and sensitivity are shown. For comparison, the sigmoidal fit line from the iodide channel is also plotted in (a) and that from the bromide channel is also plotted in (b). The systematic uncertainty derived from voltage scanning is the sum of squares of 5% uncertainty from collision limit determination and half the confidence interval of sigmoid fit divided by the corresponding fitted value.

Comment12: Page 11, lines 17-18: Is this information on fragments not something that could be utilized for other types of analyses? Not in this manuscript, but it seems like an interesting topic to explore.

Reply12. Thanks for this suggestion. We checked the signals obtained in the chamber experiments. But it is difficult for us to conclude a tendency based on this dataset. The primary problem is that we cannot establish a one-to-one correspondence between fragmentation signals and their parent compound due to the simultaneous detection of hundreds of species. To solve this problem, the most feasible approach is to design experiments that significantly reduce the number of species introduced into the instrument, thereby enabling an unambiguous elucidation of the relationship between fragmentation and their respective parent molecules. However, this is obviously out of the scope of this paper.

Comment13: Page 11, line 22: "more than 2" would be ">2".

Reply13. Thanks. We revised Page 13, Line 22 as: 'only compounds with at least 2 oxygen atoms …'. We revised Page 13, Line 26 as: 'For nitrogen-free compounds with at least 5 oxygen atoms…'.

Comment14: Page 12, line 14: I am not sure what this sentence means.

Reply14. We revised Page 14, Line 14 – 16 as: 'The signals that yielded successful voltage scanning were evaluated relative to the widely used limit-of-detection threshold of SNR = 3 (Yuan et al., 2017), in order to understand the signal strength necessary for a successful scanning.'.

Comment15: Page 14, lines 12-14: This reads as if also the latter series of compounds would have bene injected, but from later sentences, this seems not to be the case. Please make sure it is clear and correct.

Reply15. Thanks for reading carefully. We revised Page 16, Line 12 – 14 as: 'Several precursors were injected, including gasoline, biogenic, cooking, and VCP sources. During the oxidation experiments, a series of compounds that have been previously identified to be formed from certain precursors were detected.'

Comment16: Page 14, lines 18-21: What is the purpose of this sentence? If only to list the VOCs, it is unnecessarily complicated to list what they were injected as. Also, the following sentence then starts "All of these oxidation products", although they are not oxidation products.

Reply16. We removed these sentences, since the precursor-product relationships were described in the previous sentences.

Technical comments

Comment17: Page 1, Lines 3 and 21: Sensitivities of adduct ions are mentioned. Is it really the sensitivity of those that you are reporting, or is it the sensitivity of the CIMS to different molecules?

Reply17. The sensitivity we reported are all derived from calibration curves of adduct ion signal intensity versus neutral analyte concentration. Indeed, the value derived solely from the adduct ion is slightly lower than that obtained by summing the intensity of all ions originating from the analyte, including fragmentation ions and adduct ions. However, because the principle of voltage scanning is to infer sensitivity form the binding energy of the adduct formed between reagent ion and analyte, it is methodologically necessary to restrict the analysis to adduct ion alone.

Comment18: Page 1, Line 6 and elsewhere: Sensitivities are given with four significant digits in many cases. Is this possible? Given e.g. that standard gas concentrations are typically accurate to two significant digits.

Reply18. We confirm that the reported sensitivities with four significant digits are justified and reflect the precision of our calibration sources. The certified concentration on the gas cylinder label provided by the manufacturer is 6 significant digits and is gravimetrically prepared primary standards used for instrument calibration. For liquid standards and permeation tubes, the preparation involved gravimetric weighing using calibrated analytical balances with a readability of 0.1 mg, which yields four significant digits of precision.

Comment19: Page 2, lines 35 and 36. Why not simple add the year to the first mention of Lopez-Hiilfiker et al and Song et al, instead of separately adding the full citations again in the end of the sentence?

Reply19. We revised Page 2, Line 36 – 37 as: 'Lopez-Hilfiker et al. (2016) was the …Song et al. (2024) established …'

Comment20: Page 3, line 24: "SAPHIR"

Reply20. We revised Page 3, Line 28 as: 'in the SAPHIR-CHANEL campaign …'.

Comment21: Page 3, lines 40-42: Seems like some repetition from what was already said concerning definitions and acronyms.

Reply21. Corrected it. We have revised the Page 3, Line 44 – 45 in the manuscript as: 'MR-CIMS is a newly designed instrument equipped with a bipolar time-of-flight (TOF) mass spectrometer…'

Comment22: Page 5, line 3: Please rephrase "primarily purely"

Reply22. We revised this section in the revised manuscript, as replied in Reply1.

Comment23: Page 6, line 37: S4?

Reply23. Corrected it. Currently, it is Figure S5. We revised Page 7, Line 41 as 'are shown in Figure S5.'

Comment24: Page 9, line 6: Check the sentence.

Reply24. Sorry for the typo. We revised Page 11, Line 2 as: '4-nitrophenol exhibited a high dV_{50} and a sensitivity close …'

References

Riva, M., Pospisilova, V., Frege, C., Perrier, S., Bansal, P., Jorga, S., Sturm, P., Thornton, J. A., Rohner, U., and Lopez-Hilfiker, F.: Evaluation of a reduced-pressure chemical ion reactor utilizing adduct ionization for the detection of gaseous organic and inorganic species, Atmos. Meas. Tech., 17, 5887–5901, https://doi.org/10.5194/amt-17-5887-2024, 2024.